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PHASE COMPOSITION OF THE PRODUCTS OF COMBUSTION OF FERROSILICON IN NITROGEN WITH FLUORINE-CONTAINING ADDITIVES PRESENT

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The influence of fluorine-containing additives (ammonium fluoride and topaz concentrate) on the phase composition of the products of combustion of ferrosilicon in nitrogen and the morphology of the silicon nitride particles formed is investigated. It is shown that the introduction of 0.5% topaz concentrate into ferrosilicon transfers the autowave combustion regime characteristic for nitriding of ferrosilicon without additives into a layerwise regime. It is established that the high-temperature â modification of silicon nitride â-Si_3N_4 forms in the presence of ammonium fluoride and a â-Si_3N_4-based solid solution of the type SiAlON forms in the presence of the topaz concentrate.

Self-propagating high-temperature synthesis (SHS) is still a promising method for synthesizing silicon nitride, since the method is characterized by low energy-intensiveness and high productivity. The technology for obtaining silicon nitride was developed by Professor I. P. Borovinskaya and her coworkers [1, 2]. Semiconductor silicon is used as the initial material to synthesize Si_3N_4. In the SHS process silicon interacts with nitrogen according to the reaction

$$3Si + 2N_2 \rightarrow Si_3N_4 + 179.0 \text{ kcal/mole.}$$
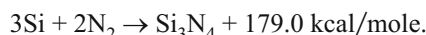
It has been shown at the Tomsk Scientific Center that in principle silicon nitride can be obtained from commercial ferrosilicon powder as well as from a dust fraction which arises when ferrosilicon is milled (RF Patent No. 2257338). Silicon nitride is separated from iron in hydrochloric acid solutions. During SHS – nitriding of ferrosilicon, which is a two-phase alloy ($FeSi_2$ + Si), the components of the initial alloy ($FeSi_2$ and Si) as well as the products of dissociation of higher-order iron silicide ($FeSi$, Fe_5Si_3, Fe_3Si) are present in the products of combustion together with the silicon nitride and α-Fe which are formed. This material finds application as an alloying component in smelting certain types of steel (RF Patent No. 2218440).

The possibility of synthesizing pure silicon nitride arises because of the need to obtain a two-component product of combustion silicon nitride – iron. In the process, SHS – nitriding must be accomplished according to the scheme

$$FeSi_2 + Si + 2N_2 \rightarrow Fe + Si_3N_4.$$

As shown in [3, 4], the composition Si_3N_4 is obtained by introducing 40 – 60%[2] pre-nitrided ferrosilicon or 1 – 10% ammonium chloride into the initial ferrosilicon.

The present article presents the results of an investigation of how fluorine-containing additives affect the phase composition of the products of combustion of ferrosilicon in nitrogen and the morphology of the silicon nitride particles which are formed.

PUD-75 ferrosilicon dust wastes with 82.0% silicon in the alloy and particle size less than 160 μm were used to synthesize silicon nitride. Chemically pure ammonium nitride and the natural mineral topaz, in amounts no greater than 3%, served as the fluorine-containing additives. Topaz $Al_2SiO_4(F, OH)_2$ is a natural fluoroalumosilicate. Topaz concentrate, from the Kopna deposit (Kemerovo Oblast), with the following composition (%) was used: 40.98 SiO_2, 34.98 Al_2O_3, 2.36 Fe_2O_3, 19.10 ($H_2O + F$), 1.40 CaO, and 1.20 MgO. The topaz content in the concentrate was about 73%, the remainder consisting of quartz. Concentrate in the form of finely dispersed yellow powder (less than 80 μm) was used. In the last few years, topaz has been actively used as a fluorinating agent and a mineralizer for obtaining ceramics [5 – 7].

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[2] Here and below — the mass content.

TABLE 1.

β-Si_3N_4 d, Å (JCPDS)	β-$Si_3Al_3O_3N_5$ d, Å (JCPDS)	Product of SHS with topaz; d, Å
3.800	3.840	3.834
3.293	3.324	3.314
2.660	2.716	2.672
2.489	2.513	2.500
2.310	2.353	2.319
2.194	2.217	2.203
2.180	2.217	2.188
1.901	1.920	1.921
1.892	1.920	1.906
1.827	1.844	1.832
1.752	1.777	1.757
1.591	1.613	1.596
1.547	1.568	1.550
1.511	1.525	1.514
1.453	1.488	1.458
1.437	1.451	1.438

Fig. 1. Exterior view of a sample combusted in the autowave (*a*) and layerwise (*b*) combustion regimes: *a*) ferrosilicon with no additives; *b*) ferrosilicon with 0.5% topaz added.

Fig. 2. Phase composition of the products of combustion of ferrosilicon in the presence of fluorine-containing additives: *a*) 1.0% topaz concentrate; *b*) 1.0% ammonium fluoride; *1*) β-Si_3N_4; *2*) α-Fe; *3*) $FeSi_2$; *4*) FeSi.

Prior to SHS, the ferrosilicon powder was dried at temperature 150 – 200°C to remove moisture and volatile impurities. The ferrosilicon powder was mixed with a fluorine-containing additive, poured into 45 – 60 mm in diameter cylindrical tubes made of a metallic mesh and combusted in nitrogen in a constant-pressure apparatus at pressure 2 – 6 MPa. The samples were ignited with a powdered igniting mixture using a tungsten spiral. After passage of the combustion front the sample was allowed to cool down completely in nitrogen and then extracted from the apparatus for subsequent investigations.

X-ray phase analysis was performed with a DRON-2 diffractometer using Co radiation. A PHILIPS SEM 515 electron microscope was used to study the morphology of the products of synthesis.

The experiments showed (Fig. 1) that the introduction of 0.5% topaz concentrate into ferrosilicon converts the autowave combustion regime, characteristic for nitriding of ferrosilicon without additives, into a layerwise regime. The propagation of the reaction wave of combustion in the layerwise regime is preferred, since combustion products with a higher degree of nitriding and uniform phase composition are formed in this case.

X-ray phase analysis established (Fig. 2) that the products of combustion consist predominantly on the high-temperature modification of silicon nitride β-Si_3N_4, iron monosilicide FeSi, and a negligible amount of the components of the initial ferrosilicon ($FeSi_2$, Si). When 0.5% topaz is added, reflections due to iron disilicide $FeSi_2$ as well as silicon Si are present in the products of combustion, while silicon reflections are not observed in the presence of 1.0% topaz but, once again, reflections due to the iron silicides $FeSi_2$ and
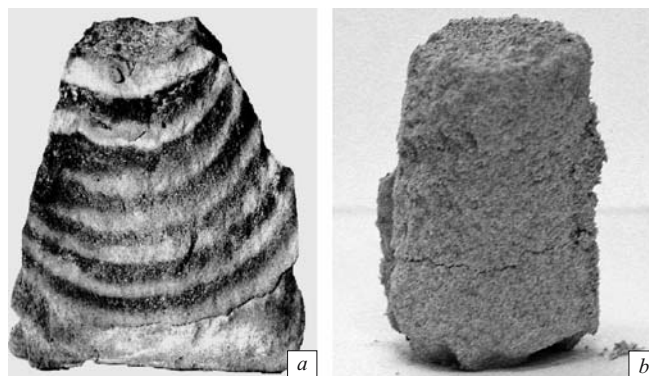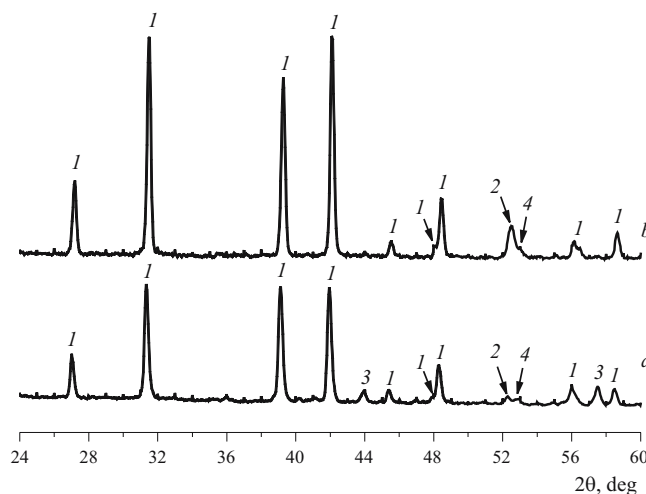
FeSi are recorded. Therefore, more complete nitriding of ferrosilicon is achieved with 1.0% topaz concentrate content.

A detailed investigation of the diffraction profile obtained for the products of combustion of ferrosilicon in the presence of 1.0% topaz additive showed a small change in the characteristics of the x-ray reflections of silicon nitride. The β-Si_3N_4 reflections are broadened, and the magnitude of the broadening is approximately the same for all lines. The position of all diffraction peaks differs from the tabulated values in the direction of smaller angles. For example, the experimentally obtained series of interplanar distances as compared with the tabulated values for β-Si_3N_4 and β-sialon with the composition $Si_3Al_3O_3N_5$ (JCPDS card catalog) occupies an intermediate position. Table 1 compares the experimental series of interplanar distances with the tabulated values for β-Si_3N_4 and sialon β-$Si_3Al_3O_3N_5$ from the JCPDS card catalog.

The data obtained show that a solid solution based on silicon nitride forms during the synthesis process.

We shall now examine the physical – chemical processes which occur during the combustion of ferrosilicon in the presence of added topaz concentrate. The main release of heat, which gives rise to the propagation of the combustion reaction wave, occurs as a result of the interaction of silicon with nitrogen. In accordance with previous results [3], the synthesis temperature can reach 2100°C. At 850 – 1000°C the topaz present ahead of the combustion front undergoes thermal decomposition with mullite $3Al_2O_3 \cdot 2SiO_2$, silica in the form of crystobalite, and hydrogen fluoride gas being formed [7]:

$$6[Al_2SiO_4(F, OH)_2] \rightarrow 2[3Al_2O_3 \cdot 2SiO_2] + 2SiO_2 + 6HF.$$

The following reaction is likely to occur at temperatures above 1000°C:

$$SiO_2 + 4HF \rightarrow SiF_4\uparrow + H_2O\uparrow.$$
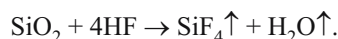
It is known that as the temperature increases above 1800°C mullite melts and decomposes with corundum precipitating.

The gaseous products which form with the thermal decomposition of topaz, breaking down the sample, promote filtration of nitrogen to the reaction zone. Silicon tetrafluoride nitrides during the combustion process with silicon nitride forming according to the reactions

$$SiF_{4(gas)} + Si_{(solid)} \rightarrow 2SiF_{2(gas)};$$

$$6SiF_{2(gas)} + 2N_2 \rightarrow Si_3N_{4(solid)} + 3SiF_{4(gas)}.$$
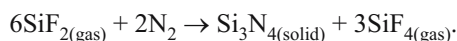
The SiF_4 newly formed in the last reaction permits the cycle to repeat and promotes nitriding through the vapor-gas phase.

After the silicon nitriding process has been completed, silicon tetrafluoride interacts with iron in the nitrogen atmosphere with iron trifluoride forming:

$$3SiF_4 + 4Fe + 2N_2 \rightarrow Si_3N_4 + 4FeF_3,$$
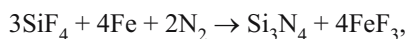
which was found in the surface layers of the burned sample and on the walls of the SHS apparatus.

The results of an investigation of the microstructure of the combustion products (Fig. 3), consisting of $1 – 2\ \mu m$ in diameter and up to $10\ \mu m$ long crystals with prismatic habitus, also show that vapor-gas mass transfer plays a large role during nitriding of ferrosilicon in the presence of the topaz concentrate. X-ray spectral microanalysis of the crystals showed that Al is present in them together with Si, which together with the XPA results indicates formation of a solid solution based on silicon nitride.

The addition of 1.0% ammonium fluoride to ferrosilicon gives more complete nitriding (0.95) than adding 1.0% topaz concentrate (0.80). The results of XPA (see Fig. 2b) show that in the presence of ammonium fluoride the products of
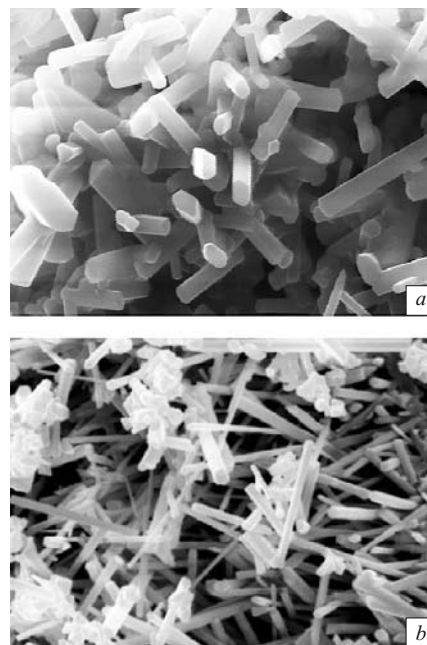

Fig. 3. Microstructure of the products of nitriding of ferrosilicon in the presence of fluorine-containing additives: a) 1.0% topaz concentrate (× 5000); b) 1.0% ammonium fluoride (× 4780).

combustion do not contain components of the initial ferrosilicon $FeSi_2$ and Si, and the reflections of the β-modification of silicon nitride and α-Fe are much more intense than the corresponding reflections observed in the presence of the topaz concentrate. The more complete nitriding in the presence of added ammonium fluoride is due to the fact that the ammonium fluoride ahead of the combustion front decomposes into ammonia and hydrogen fluoride:

$$NH_4F \rightarrow NH_3\uparrow + HF\uparrow.$$

The ammonia released as a result of the reaction is an additional nitriding agent. It is well known that when ammonia dissociates, some nitrogen molecules are in a more active state, which results in a higher nitriding rate. The addition of ammonium fluoride intensifies predominately the nitriding of iron silicides, which is completed by the formation of silicon nitride and the precipitation of iron. Fluorine is present in the form of iron trifluoride in the products of combustion, and it is subsequently removed from the target product by acidic enrichment.

As the experiments showed, a complex additive consisting of 1 – 3% topaz concentrate and 1% ammonium fluoride must be used to attain the highest possible degree of nitriding of ferrosilicon. A similar result was obtained by introducing 1% topaz concentrate and 40 – 50% pre-nitrided ferrosilicon (Fe – Si – N) into the initial charge. In both cases, the products of combustion consist of Si_3N_4 + Fe, which can be subjected to acidic enrichment in a solution of hydrochloric acid to remove the iron.

It should be noted that the products of combustion of ferrosilicon in nitrogen in the presence of topaz consist of a loose, essentially unsintered, material which easily crumbles. Consequently, such a material does not need to be ground in a ball mill, in contrast to the products of nitriding a ferrosilicon to which ammonium fluoride has been added (the material is adequately sintered and must be milled).

In summary, complex additives must be used in order to attain the maximum possible degree of nitriding: $1 - 3\%$ topaz concentrate $+ 1\%$ ammonium fluoride or 1% topaz concentrate and $40 - 50\%$ pre-nitrided ferrosilicon. The high-temperature β-modification of silicon nitride β-Si_3N_4 forms in the presence of ammonium fluoride, and a β-Si_3N_4-based solid solution of the type SiAlON is formed in the presence of added topaz concentrate, which must be taken into account when developing ceramic materials.

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